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PHYSICAL – CHEMICAL PROPERTIES OF LOW-MELTING GLAZES OPACIFIED BY FLOTATION TAILINGS FROM A COPPER-ENRICHMENT PLANT

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The results of synthesis of low-melting opacified glazes for household ceramics based on the system R_2O – RO – B_2O_3 – Al_2O_3 – Fe_2O_3 – ZnO – SiO_2, which possesses high heat and chemical resistance, are presented. The interrelation of the physical-chemical properties and the phase composition and structure of the coatings with different content of the flotation tailings introduced are investigated.

Finding ways to solve environmental protection problems, developing waste-free and resource-conserving technologies, and salvaging industrial wastes are all topical problems in modern materials engineering.

We have investigated the possibility of using flotation tailings from the copper-enrichment plant (CEP) of the Almalyk Mining and Metallurgical Works (AMMW) to obtain zirconium-free opacified glazes possessing high opacification power, luster, microhardness, and heat and chemical resistance.

The physical – chemical properties and crystallization power of glaze frits and coatings, which contain flotation tailings from CEP of AMMW were studied.

The CEP flotation tailings are formed when copper-containing ore is enriched and it consists of a dark grey aluminum – iron silicate compound. The results of the analysis showed that the chemical composition of the samples of CEP tailings obtained at different times of the year is virtually identical (%[2]): 61.20 – 65.25 SiO_2, 11.89 – 13.57 Al_2O_3, 5.70 – 9.17 Fe_2O_3, 1.00 – 1.96 CaO, 1.58 – 2.81 MgO, 0.67 – 1.56 Na_2O, 4.54 – 5.80 K_2O, 1.88 – 5.93 SO_3, 3.90 – 4.54 calcination loss.

The main mineral components of the tailings studied are quartz (up to 44%), feldspar (up to 9%), hydromica (up to 22%), as well as gypsum and calcium and magnesium carbonates (about 3%) [1].

The CEP flotation tailings have a finely dispersed granulometric composition, and their melting temperature is 1220 – 1230°C.

Five compositions of glazes with 20 – 40% CEP flotation tailings were studied. The initial system for synthesis of the glazes was R_2O – RO – B_2O_3 – Al_2O_3 – Fe_2O_3 – ZnO – SiO_2. The content of alkali oxides ($Na_2O + K_2O$) in the optimal compositions was 5.68 – 6.54%, ZnO — 3.12 – 3.20, SiO_2 — 45.96 – 46.06, alkali-earth oxides (CaO + MgO) — 17.09 – 19.06, B_2O_3 — 14.07 – 14.78%.

The frit was melted in 0.5 liter chamotte crucibles in a Silit electric furnace at 1350 – 1400°C with a holding period at the maximum temperature of 1.0 – 1.5 h until a uniform glass mass was obtained. The granular frit melted uniformly and its opacity was low. The green-brown frits easily flowed together, forming a long, thin, knot-free filament.

The glaze suspensions were prepared by the wet method with the introduction of 5% angren fire clay, sieved to residue 0.6 – 0.8% on a No. 0063 sieve. The density of the suspension was 1450 – 1530 kg/m^3.

The intermediate product of majolica articles from the Tashkent Experimental and Applied-Art Works, which went through their first calcination at 850 – 900°C and whose water absorption was 17 – 20%, was used for glazing. The articles were glazed by means of pulverization, poring, and dipping. The glaze layer was dried under natural conditions, after which the articles were calcinated in electric furnaces at 900 – 950°C. After calcination, the coatings flowed uniformly and possessed uniform mirror-like luster as well as good opacification and coverage of the articles. The results of the physical – chemical studies are presented in Table 1.

After the second calcination all glazed samples, irrespective of the content of flotation tailings (20 – 40%), showed complete opacification. The coatings were pale brown and had no crack networks.

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[2] Here and below: mass content.

As one can see, glaze is easily adapted for manufacturing and it is distinguished by high performance and decorative indicators. The microhardness of the samples increases from 5.8 to 6.3 kg/m^2 with increasing content of the CEP flotation tailings.

It has been determined from the crystallizability data for glaze frits that surface opalescence is observed at 700°C, a crystalline film at 750°C, a thin crystalline crust at 800°C, complete crystallization at 880°C, and melting of crystals at 950°C.

The phase composition and structure of frit and coatings heat-treated at different temperatures was studied to determine the glaze formation mechanisms. According to x-ray phase analysis, the frit of a glaze containing 25% flotation tailings from copper ores and with a constant content of borax, chalk, and zinc contains a small amount of the crystalline phase of anortite with the characteristic lines of interplanar distances (d = 0.376, 0.322, and 0.246 nm). As the tailings content increases further to 40%, a mixture of wollastonite (d = 0.300, 0.320, 0.222, and 0.198 nm), diopside (d = 0.298 and 0.251 nm), and anortite crystals starts to precipitate.

In glazes containing up to 40% CEP flotation tailings, crystals of diopside and wollastonite precipitate and the intensity of the anortite lines increases. So, the crystalline phase $CaSiO_3$ is identified at temperatures 650 – 750°C, and the amount of this phase is negligible and shows virtually no increase as compared with the data of the diffraction pattern obtained for the glaze frit.

An appreciable increase of the diffraction peaks of wollastonite $CaSiO_3$ is observed at temperatures from 750 to 850°C, and then the amount of $CsSiO_3$ remains practically constant up to 950°C, at which temperature maxima due to anortite $CaAl_2Si_2O_3$ and diopside $CaMgSi_2O_6$ appear.

One exothermal effect with a maximum at 830 – 850°C is observed on the DTA curves. As the flotation tailings content increases, this maximum shifts in the direction of low temperatures and the height of the exothermal peak increases (Fig. 1).

The IR spectroscopic studies (Fig. 2) of frit showed the presence of a quite intense absorption band with a maximum at 980 – 1100 cm^{-1} as well as weaker bands (1385, 800, 750, 700, and 680 cm^{-1}). The position of the main absorption band in the range 980 – 1100 cm^{-1} shows that groupings close to the framework are present in the structure of the glass. The presence of an additional band near 980 cm^{-1} can be attributed to the formation of Si – O – Me non-bridge bonds in groupings of the type metal and orthosilicates [2].

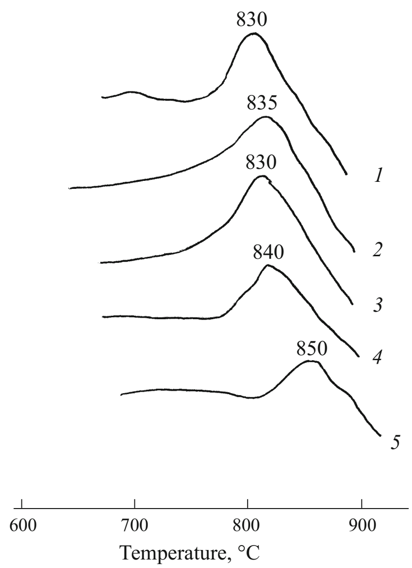

Fig. 1. DTA curves of glazes with different content of CEP flotation tailings. The numbers on the curves correspond to the numbers of the glazes.

The wide absorption band in the high-frequency range of the spectrum at 1400 cm^{-1} is due to the vibrations of the bonds of the three-fold coordinated boron atoms in the complex with polymerized groups [BO_3]. It is well known that in silicates containing boron in tetrahedral coordination the region of intense absorption is shifted to lower frequencies and coincides with the vibrations of the [SiO_4] groups, making it difficult to identify them.

According to the published data [2], the absorption in the frequency range 700 – 800 cm^{-1} is due to the presence of aluminum – oxygen tetrahedra. The presence of an absorp-

TABLE 1.

Glaze	Mass content in the CEP flotation tailings frit, %	Fusibility, °C	Softening temperature, °C	CLTE, 10^{-7} K^{-1}			Average value, %		Chemical resistance of crystallized frits, %	
				computed data (Appen)	experimental values		reflection coefficient	luster	in 20% HCl	in 2 N NaOH
					at temperature 400°C	at softening temperature				
1	40	910 – 970	660	62.68	64.86	69.36	52	43	99.97	99.85
2	35	890 – 960	590	62.98	65.07	70.45	48	46	99.97	99.86
3	30	880 – 960	580	63.66	65.38	70.32	46	45	99.98	99.88
4	25	760 – 810	560	63.40	64.61	69.47	45	51	99.97	99.86
5	20	740 – 790	550	61.56	63.03	67.90	42	58	99.97	99.78

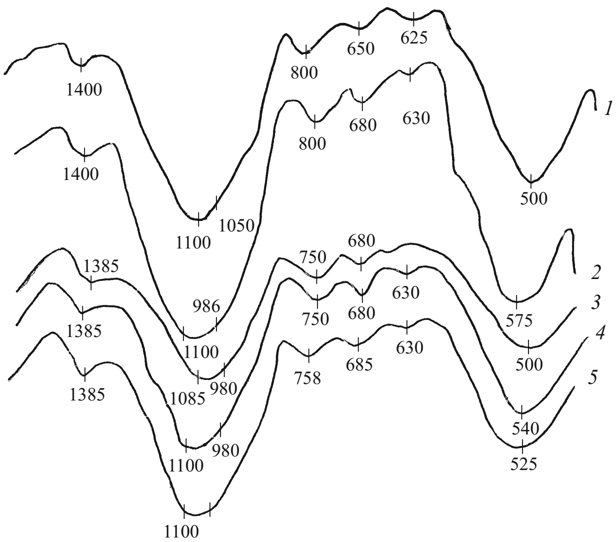

Fig. 2. IR absorption spectra (cm^{-1}) of opacified glazes with different content of CEP flotation tailings. The numbers on the curves correspond to the numbers of the glazes.

tion band at 680 cm^{-1}, which is characteristic for [AlO_6] tetrahedra, gives a basis for asserting that the aluminum in the compositions studied is four-fold coordination, isomorphically substituting for silicon with formation of a mixed aluminum – silicon – oxygen framework, as well as six-fold coordination, not participating in the construction of the structure of the glass network but playing the role of a modifying agent. The appearance of absorption in the range 750 – 800 cm^{-1} can be explained by the presence of quartz in glazes [2].

The main absorption band at 1100 cm^{-1} remains in practically the same position but its intensity changes appreciably, i.e., the spectra become more extended and the maximum at 980 cm^{-1} flattens out. This shows that the degree of polymerization of the silicon – oxygen groupings remains quite high. On the whole the spectra acquire a form that is characteristic of a crystallized substance. XPA confirmed the increase of the degree of crystallization of the glaze and the increase of the amount of crystalline phases up to 950°C.

In summary, these investigations have shown that opacified glazes, distinguished by good eutectic properties and high physical – chemical indicators with 20 – 40% content of the CEP flotation tailings, can be obtained on the basis of the system $R_2O – RO – B_2O_3 – Al_2O_3 – ZnO – SiO_2$.

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